is dipole-allowed for the planar acyclic tetrazene. This agrees with the absorption spectrum observed for **3**, whose lowest energy absorption at 312 nm or 3.97 eV (ϵ = 21 000) matches well with the 3.95 eV calculated for the HOMO–LUMO transition in $(H_3Si)(H)N_4(H)(SiH_3)$. A similar assignment has been proposed for the lowest energy absorption in N_4H_4 (4.7 eV)[20] and other tetrazenes.[21] The only other transition, found at 258 nm or 4.81 eV (ϵ = 21 000) in the absorption spectrum of **3** probably results from the characteristic[22] π–π^* transitions of the two phenyl substituents in **3**. For $H_2SiN(H)NNN(H)$ the $3b_1 \rightarrow 2a_2$ $(\pi_3 \rightarrow \pi_4)$ HOMO–LUMO transition is predicted to be blue shifted from that in the linear isomer. Again there is good agreement between the calculated value of 4.35 eV and the experimental value for **6** (302 nm or 4.11 eV ($\epsilon \sim$ 20 000)). Assignment of the three other intense features in the UV spectrum of **6** (at 4.41, 5.60, and 6.02 eV) is problematic since both the $6b_2 \rightarrow 2a_2$, $1a_2 \rightarrow 2a_2$ transitions, and those originating from the phenyl substituents should occur in this region. The photochemical activity toward fragmentation of the N_4 group noted earlier is consistent with the antibonding character of the $3b_g$ or $2a_2$ orbital populated on electronic excitation.

Acknowledgment. This work is based on research sponsored by the Air Force Office of Scientific Research, Air Force Systems Command, USAF, under Grant AFOSR-86-0027. We thank the DoD University Research Instrumentation Program (Grant DAAL03-87-G-0071) for funds to purchase an X-ray diffractometer.

Registry No. 1, 109719-17-7; **2**, 4147-89-1; **3**, 118399-12-5; **5**, 118399-13-6; **6**, 109639-46-5; **7**, 3284-06-8; **8**, 109639-47-6; Me_3SiCl, 75-77-4; Me_2SiCl_2, 75-78-5; Me_3GeCl, 1529-47-1; $PhN(GeMe_3)_2$, 13361-71-2.

Supplementary Material Available: Tables of positional parameters for hydrogen atoms, thermal parameters, and bond angles for these complexes (9 pages); listings of observed and calculated structure factors (20 pages). Ordering information is given on any current masthead page.

---

[21] Wiberg, N.; Vasisht, S. K.; Bayer, H.; Meyers, R. *Chem. Ber.* **1979**, *112*, 2718.

[22] Dyer, J. R. *Applications of Absorption Spectroscopy of Organic Compounds*; Prentice-Hall: New York, 1965; p 18.

Base-Induced Migrations of Germyl, Stannyl, and Plumbyl Groups to the Cyclopentadienyl Ligand in the System $(\eta^5\text{-}C_5H_5)M(CO)_nER_3$ (M = Fe, Mo, W; *n* = 2, 3; E = Ge, Sn, Pb; R = Me, Ph)[1]

Jorge Cervantes,[†] Steven P. Vincenti,[‡] Ramesh N. Kapoor,[‡] and Keith H. Pannell*[,‡]

Departments of Chemistry, Universidad Autonoma Metropolitana, Iztapalapa, Mexico D.F., Mexico, and The University of Texas at El Paso, El Paso, Texas, 79968

Received July 26, 1988

Treatment of the general class of complex $(\eta^5\text{-}C_5H_5)M(CO)_nER_3$ (M = Fe, Mo, W; *n* = 2, 3; E = Ge, Sn, Pb; R = Me, Ph) with lithium diisopropylamide (LDA) gives rise to deprotonation of the cyclopentadienyl ring followed by migration of the ER_3 group to the cyclopentadienyl ring. The resulting metalate anion may be quenched with methyl iodide to yield $(\eta^5\text{-}C_5H_4ER_3)M(CO)_nMe$. In the case of the EPh_3 complexes this is the only chemistry observed for all three transition metals and group 14 elements, with the exception of $(\eta^5\text{-}C_5H_5)Fe(CO)_2PbPh_3$. For the trimethyl derivatives only the Ge complexes undergo this chemistry in high yield, while the Sn and Pb complexes exhibit both the migration reaction and direct base-induced cleavage of the transition metal–Sn(Pb) bond to yield the transition metalate $[(\eta^5\text{-}C_5H_5)M(CO)_n]^-$. The use of *n*-butyllithium in place of LDA produces considerably more M–E cleavage except for the germanium complexes where migration chemistry is observed.

Introduction

In the course of a study on the formation of carbene derivatives of molybdenum and tungsten containing germanium and tin, Dean and Graham observed that migrations of Ph_3Ge groups from both Mo and W to the cyclopentadienyl ring in the system $(\eta^5\text{-}C_5H_5)M(CO)_3GePh_3$ (M = Mo, W) occurred upon reaction of the complexes with alkyllithium reagents.[2] The degree that such migrations were observed depended upon the basicity of the alkyllithium. When *tert*-butyllithium was used significant amounts of migration were observed, especially when the metalate anions formed were trapped with $(CH_3)_3OPF_6$, whereas with methyllithium only methoxycarbene complexes were obtained upon quenching, e.g. $(\eta^5\text{-}C_5H_5)Mo(CO)_2(GePh_3)C(OMe)Me$. Related alkoxycarbene derivatives of triphenyltin complexes were also synthesized, but no tin migrations to the cyclopentadienyl ring were observed.

Following the Dean and Graham report several groups have studied such reactions. It has been shown that related base-induced migrations occur with silyl,[3,4] oligosilyl,[5]

[†] Universidad Autonoma Metropolitana.

[‡] The University of Texas at El Paso.

[1] Organometalloidal Derivatives of the Transition Metals. 19. For part 18 see: Pannell, K. H.; Rozell, J. R.; Lii, J.-C.; Tien-Mayr, S.-Y. *Organometallics*, in press.

[2] Dean, W. K.; Graham, W. A. G. *Inorg. Chem.* **1977**, *16*, 1060.

[3] Berryhill, S. R.; Clevenger, G. L.; Burdurli, Yu. P. *Organometallics* **1985**, *4*, 1509.

[4] Thum, G.; Riews, W.; Greissinger, D.; Malisch, W. *J. Organomet. Chem.* **1983**, *252*, C67.

[5] Pannell, K. H.; Cervantes, J.; Hernandez, C.; Cassias, J.; Vincenti, S. P. *Organometallics* **1986**, *5*, 1056.

0276-7333/89/2308-0744$01.50/0 © 1989 American Chemical Society

acyl,[6,7] and hydrido[8] cyclopentadienyl metal complexes. In such reactions initial deprotonation of the cyclopentadienyl ring occurs followed by the migration of the group bonded to the metal center to generate a metal-localized anion that may be quenched with a variety of species. When the group bonded to the transition-metal center is an alkyl group, no migrations occur,[6,3,9] and the cyclopentadienyl localized anion may be trapped with, for example, methyl iodide. In the particular case that the alkyl group is a disilylmethyl group a migration occurs involving internal nucleophilic attack on the α-silicon atom resulting in a migration with rearrangement.[9]

It has been shown that these migrations are intramolecular,[3,6] involve retention of configuration at the metal center,[6] and retention of configuration of a migrating silyl group.[10] The generality of this reaction has not been exhaustively examined, however, a potentially useful series of organometallic reactions is available. To date no examples of tin or lead migrations have been reported.

In the present study we have investigated the ability of LDA and *n*-BuLi to effect migrations of Ge, Sn, and Pb groups from Fe, Mo, and W metal centers to cyclopentadienyl rings. The study illustrates the ready migration of triphenylgermanium, -tin, and -lead groups for the metals studied and the more limited migration of the trimethyl derivatives. Cleavage of the transition metal–group 14 element bond was also observed in some cases, especially with the more basic *n*-BuLi.

Experimental Section

All reactions were performed under inert atmospheres, N_2 or Ar, using dry oxygen free solvents and reagents. Infrared spectra were recorded on a Perkin-Elmer 580B spectrophotometer and NMR spectra on an IBM NR 200 multinuclear spectrometer. Starting complexes $[(\eta^5\text{-}C_5H_5)M(CO)_nER_3]$ were synthesized by using standard published procedures.[11,12] LDA was used freshly prepared, and *n*-BuLi was purchased from commercial sources and used without prior purification. Elemental analyses were performed by Galbraith Laboratories Inc., Knoxville, TN.

The same general reaction procedure was utilized for all systems studied. Representative examples of the use of both LDA and *n*-BuLi are provided below.

Synthesis of $(\eta^5\text{-}C_5H_4SnPh_3)Mo(CO)_3Me$. To a magnetically stirred solution of $(\eta^5\text{-}C_5H_5)Mo(CO)_3SnPh_3$ (1.0 g, 1.7 mmol) in 50 mL of THF at 0 °C was added dropwise LDA (4.0 mL, 2.24 mmol in THF). There was an immediate color change from pale yellow to orange. Monitoring by IR indicated that after 1 h the starting material had disappeared and been replaced by a species with infrared stretching CO frequencies at 1905, 1806, 1782, and 1716 cm^{-1}. An excess of methyl iodide was then added and with stirring permitted to warm to room temperature. At this time the solvent was removed under vacuum and the residue extracted with a 70:30 hexane/methylene chloride solvent mixture. The solution was filtered and again the solvent removed under vacuum to leave a yellow solid material. This solid was dissolved in the minimum of methylene chloride and placed upon an alumina column, 2.5 × 20 cm. Elution with a 90:10 hexane/methylene chloride solvent mixture developed a yellow band which was collected. Recrystallization from the same solvent composition yielded $(\eta^5\text{-}C_5H_4SnPh_3)Mo(CO)_3Me$ (0.41 g, 40%) as a yellow solid. The melting point, elemental analysis, and spectral data of the product and those of all the other new complexes are recorded in Tables I and II.

Table I. Yields and Analytical Data for $(\eta^5\text{-}C_5H_4ER_3)M(CO)_nMe$ Complexes

			anal. calcd (found)	
complex	% yield[a]	mp,[b] °C	C	H
		E = Ge		
R = Me, M = Fe	30	[c]	47.8 (47.7)	5.22 (5.31)
R = Me, M = Mo	30	61–62	38.3 (38.0)	4.28 (4.56)
R = Me, M = W	52	47–48	31.0 (30.9)	3.49 (3.61)
R = Ph, M = Fe	30	112–113	63.1 (62.9)	4.48 (4.82)
		E = Sn		
R = Me, M = Fe	60	[c]		
R = Ph, M = Fe	61	71–74	57.7 (57.8)	4.10 (4.33)
R = Ph, M = Mo	40	110–111	53.2 (53.2)	3.64 (3.87)
R = Ph, M = W	68	108–109	46.5 (47.1)	3.18 (3.46)
		E = Pb		
R = Ph, M = Mo	68	92–94	46.5 (46.1)	3.17 (3.07)
R = Ph, M = W	63	116–117	41.2 (40.5)	2.82 (2.87)

[a] Nonoptimized recovered yields. [b] Uncorrected. [c] Oil.

Synthesis of $(\eta^5\text{-}C_5H_4GeMe_3)Fe(CO)_2Me$. To a THF solution (50 mL) of $(\eta^5\text{-}C_5H_5)Fe(CO)_2GeMe_3$ (0.5 g, 1.7 mmol) was added 4.0 mL of a LDA solution (2.24 mmol in THF) at 0 °C. The solution was stirred for 1 h at which time the ν(CO) bands for the starting complex had been replaced by bands at 1878, 1867, 1811, and 1749 cm^{-1} typical of a cyclopentadienyl dicarbonyliron anion system. To this solution was added an excess of methyl iodide and the solution was stirred for 10 min prior to solvent removal under vacuum. The residue was placed upon an alumina column, 2.5 × 15 cm, and eluted with hexane to develop a yellow band that was recovered. From this solution was isolated a 60% yield of $(\eta^5\text{-}C_5H_4GeMe_3)Fe(CO)_2Me$.

Synthesis of $(\eta^5\text{-}C_5H_4PbPh_3)W(CO)_3Me$. To a THF solution (50 mL) of $(\eta^5\text{-}C_5H_5)W(CO)_3PbPh_3$ (1.0 g, 1.3 mmol) was added 4.0 mL of a LDA solution (2.24 mmol in THF) at 0 °C. The solution was stirred for 20 min at which time an infrared spectrum indicated that all the starting material had been consumed and replaced by a species with ν(CO) at 1905, 1809, 1787 (sh), and 1722 cm^{-1} indicative of a metal-localized tungsten cyclopentadienyl tricarbonylate. Addition of an excess of methyl iodide followed by stirring for 10 min produced a species with ν(CO) at 2011 and 1915 cm^{-1}. The solvent was removed under vacuum and the solid residue extracted with a 50:50 methylene chloride/hexane solvent mixture. This solution was filtered, concentrated, and placed upon an alumina column, 2.5 × 20 cm. Elution with a 30:70 methylene chloride/hexane solvent mixture developed a yellow band from which after recrystallization yielded 0.65 g (63%) of $(\eta^5\text{-}C_5H_4PbPh_3)W(CO)_3Me$.

Treatment of $(\eta^5\text{-}C_5H_5)W(CO)_3SnMe_3$ with *n*-BuLi. A solution of $(\eta^5\text{-}C_5H_5)W(CO)_3SnMe_3$ (1.0 g, 2.0 mmol) in 50 mL of THF was treated with a slight excess of a hexane solution of *n*-BuLi. The solution was stirred for 1 h at which time infrared monitoring indicated that only a tungsten cyclopentadienyl tricarbonylate was present. This solution was worked up in the manner described above to yield a semisolid crude reaction product. NMR analysis of this crude product indicated the presence of $Me_3Sn\text{-}n\text{-}C_4H_9$ and $(\eta^5\text{-}C_5H_5)W(CO)_3Me$. Purification via column chromatography, and elution with hexane, resulted in the isolation of $(\eta^5\text{-}C_5H_5)W(CO)_3Me$ (70%). Spectral properties were identical with those of an authentic material.

Treatment of $(\eta^5\text{-}C_5H_5)Mo(CO)_3SnMe_3$ with LDA. To a stirred THF (50-mL) solution of $(\eta^5\text{-}C_5H_5)Mo(CO)_3SnMe_3$ (0.77 g, 1.9 mmol) at 0 °C was added a solution of LDA (4.0 mL, 2.24 mmol in THF). The solution was stirred for 15 min at which time the starting material had been consumed and a species with ν(CO) at 1906, 1807, 1783, and 1718 cm^{-1} was present. To this solution was added an excess of methyl iodide. Workup as above yielded a crude reaction product that was analyzed by NMR to be a mixture of $(\eta^5\text{-}C_5H_5)Mo(CO)_3Me$ and $(\eta^5\text{-}C_5H_4SnMe_3)Mo(CO)_3Me$ in the ratio 90:10. The crude mixture was placed upon an alumina column, 2.5 × 15 cm, and eluted with hexane. A yellow band developed that was collected and shown to contain the same ratio

---

(6) Heah, P. C.; Gladysz, J. A. *J. Am. Chem. Soc.* **1984**, *106*, 7636.

(7) Abbott, S.; Baird, G. J.; Davies, S. G.; Dordor-Hedgecock, I. M.; Maberly, T. R.; Walker, J. C.; Warner, P. *J. Organomet. Chem.* **1985**, *289*, C17.

(8) Crocco, G. L.; Gladysz, J. A. *J. Chem. Soc., Chem. Commun.* **1985**, 283.

(9) Pannell, K. H.; Vincenti, S. P.; Scott, R. C., III. *Organometallics* **1987**, *6*, 1593.

(10) Berryhill, S. R.; Corriv, R. J. P. *J. Organomet. Chem.*, in press.

(11) Gorsich, R. D. *J. Am. Chem. Soc.* **1962**, *84*, 2486.

(12) Patil, H. R. H.; Graham, W. A. G. *Inorg. Chem.* **1966**, *5*, 1401.

Table II. Spectral Properties of (η^5-$C_5H_4ER_3$)$M(CO)_nMe^a$ Complexes

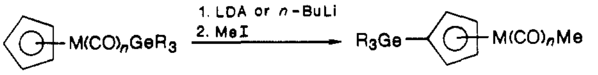
	E = Ge
	R = Me, M = Fe
^1H	0.39 (Me_3Ge), 0.5 (FeMe), 4.2, 4.4 (η^5-C_5H_4)
^{13}C	−22.8 (Fe–Me), −1.1 (Me_3Ge), 87.2, 92.1 (η^5-C_5H_4), 217.8 (CO)
ν(CO)	2010, 1954
	R = Me, M = Mo
^1H	0.33 (Me_3Ge), 0.57 (MoMe), 4.68, 4.85 (η^5-C_5H_4)
^{13}C	−21.7 (MoMe), −0.71 (Me_3Ge), 92.5, 96.6, 97.2 (η^5-C_5H_4), 227.8 (CO)
ν(CO)	2021, 1936, 1904
	R = Me, M = W
^1H	−0.2 (Me_3Ge), 0.2 (WMe), 4.5, 4.7 (η^5-C_5H_4)
^{13}C	−34.5 (WMe), −0.04 (Me_3Ge), 95.6, 95.5 (η^5-C_5H_4), 217 (CO)
ν(CO)	2018, 1927, 1894
	R = Ph, M = Fe
^1H	0.3 (FeMe), 4.49, 4.55 (η^5-C_5H_4), 7.3–7.7 (Ph)
^{13}C	−22.3 (FeMe), 85.9, 89.0, 92.3 (η^5-C_5H_4), 218 (CO)
ν(CO)	2013, 1957
	E = Sn
	R = Me, M = Fe
^1H	0.29 (Me_3Sn), 0.34 (FeMe), 4.4, 4.5 (η^5-C_5H_4)
^{13}C	−22.8 (FeMe), −8.85 (Me_3Sn), 85.0, 87.7, 94.3 (η^5-C_5H_4), 218.0 (CO)
ν(CO)	2009, 1952
	R = Me, M = Mo
^1H	0.14 ($SnMe_3$), 0.43 (MoMe) (spectrum run in C_6D_6)
^{13}C	−21.9 (MoMe), −8.57 (Me_3Sn), 94.0, 97.3, 99.0 (η^5-C_5H_4), 227.8 (CO)
ν(CO)	2021, 1934
	R = Me, M = W
^1H	0.13 (SnMe), 0.51 (WMe), 4.5, 4.8 (η^5-C_5H_4)
^{13}C	−34.5 (WMe), −8.32 (Me_3Sn), 92.5, 96.4, 97.4 (η^5-C_5H_4), 217.5 (CO)
ν(CO)	2018, 1924
	R = Ph, M = Fe
^1H	0.06 (FeMe), 4.8, 4.9 (η^5-C_5H_4), 7.2–7.7 (Ph)
^{13}C	−22.6 (FeMe), 88.6, 93.9 (η^5-C_5H_4), 128.7, 129.3, 136.5 (Ph), 217.0 (CO)
ν(CO)	2011, 1957
	R = Ph, M = Mo
^1H	0.26 (MoMe), 5.2, 5.6 (η^5-C_5H_4), 7.3–7.6 (Ph)
^{13}C	−21.7 (MoMe), 92.5, 96.9, 99.6 (η^5-C_5H_4), 128.7, 129.5, 136.9 (Ph), 226.2 (CO)
ν(CO)	2019, 1929
	R = Ph, M = W
^1H	0.28 (WMe), 5.2, 5.6 (η^5-C_5H_4), 7.3–7.7 (Ph)
^{13}C	−34.4 (WMe), 91.5, 96.0, 98.0 (η^5-C_5H_4), 128.0, 136.0 (Ph), 215.6 (CO)
ν(CO)	2017, 1922
	E = Pb
	R = Me, M = Mo
^1H	0.3 (MoMe), 0.9 ($PbMe_3$), 5.0, 5.2 (η^5-C_5H_4)
^{13}C	−21.7 (MoMe), 0.31 (Me_3Pb), 92.8, 99.8, 100.3 (η^5-C_5H_4), 227.1 (CO)
ν(CO)	2018, 1932
	R = Me, M = W
^1H	0.3 (WMe), 0.9 (WMe), 5.1, 5.5 (η^5-C_5H_4)
^{13}C	−34.9 (WMe), 0.32 (Me_3Pb), 92.3, 95.6, 98.4 (η^5-C_5H_4), 216 (CO)
ν(CO)	2017, 1924
	R = Ph, M = Mo
^1H	0.29 (MoMe), 5.3, 5.5 (η^5-C_5H_4), 7.3–7.7 (Ph)
^{13}C	−21.1 (MoMe), 97.4, 100.4 (η^5-C_5H_4), 129.0, 130.0, 138.0, 149.0 (Ph), 227 (CO)
ν(CO)	2021, 1938
	R = Ph, M = W
^1H	0.21 (WMe), 5.3, 5.7 (η^5-C_5H_4), 7.4–7.7 (Ph)
^{13}C	−34.7 (WMe), 92.5, 96.0, 98.0, 104.0 (η^5-C_5H_4), 128.0, 129.0, 137.0 (Ph), 216 (CO)
ν(CO)	2018, 1928

[a] NMR spectra were recorded in $CDCl_3$ and IR spectra in hexane. Chemical shifts in δ and ν(CO) in cm^{-1}.

of complexes. The overall yield of the recovered mixture was 0.40 g (81%). Attempts to purify the mixture via removal by sublimation of (η^5-C_5H_5)$Mo(CO)_3Me$ permitted concentration of the minor product but with progressively decreasing amounts of material.

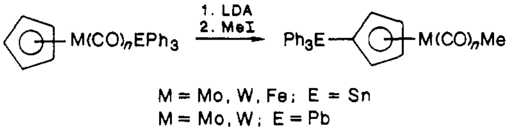
Results and Discussion

Of the three group 14 element complexes investigated in this study only the germanium complexes were uniformly found to undergo the metal to cyclopentadienyl ring migration. Thus, trimethylgermyl and triphenylgermyl derivatives of the three transition-metal systems studied, (η^5-C_5H_5)$M(CO)_n$– (M = Fe (n = 2) and Mo and W (n = 3)), readily undergo the migration reaction (eq 1). This was true when either LDA or the more basic n-BuLi was utilized. In the latter case for the Mo and W systems infrared monitoring of the solutions prior to purification via column chromatography indicated small, 5–10%, amounts of carbene complexes of the type noted by Dean and Graham.[2] No attempt was made to isolate these complexes, and they apparently decompose during the chromatographic purification process used in this study. In general the unoptimized recovered yields of the migrated products ranged from 30 to 70%.



(1)

Migration products derived from the stannyl and plumbyl complexes were more difficult to obtain. In the case of Ph_3Sn and Ph_3Pb tungsten and molybdenum complexes clean migration from the metal to the cyclopentadienyl ring resulted in moderate to good yields when LDA was used as the base (eq 2). The same result was observed with (η^5-C_5H_5)$Fe(CO)_2SnPh_3$.



(2)

Attempts to perform the same reaction in the case of the lead complex (η^5-C_5H_5)$Fe(CO)_2PbPh_3$ were complicated by side reactions that are unclear at this time. No clean metalate anion spectra were obtained upon addition of LDA, and a mixture of several materials, including a $PbPh_3$ migration product, was obtained upon quenching with MeI.

In the case of the trimethyltin and -lead complexes treatment with LDA did not result in clean reactions. In all cases subsequent to the formation of metalate ions and quenching with methyl iodide a mixture of products was obtained. The EMe_3 migration product was observed along with a product derived from cleavage of the transition metal–group 14 metal bond, i.e. (η^5-C_5H_5)$M(CO)_nMe$. The relative amounts of the two products varied depending upon both the transition metal and ER_3 systems used. In the case of (η^5-C_5H_5)$Fe(CO)_2SnMe_3$ 95% of the Me_3Sn migration product was obtained, the highest relative amount of migrated product observed. In this case although separation of the two products via column chromatography was not possible, the non-tin-containing product could be removed from a mixture by sublimation. In contrast, with (η^5-C_5H_5)$W(CO)_3PbMe_3$ only 30% of the corresponding migration product was observed. In this reaction it was not possible to separate the two products, a state of affairs repeated for the remainder of the Me_3Pb and Me_3Sn derivatives. Spectral properties of the migration products were thus obtained from mixtures con-

Table III. Relative Amounts of Migration and Cleavage upon Treatment of $(\eta^5\text{-}C_5H_5)M(CO)_nEMe_3$ with LDA[a]

	$(\eta^5\text{-}C_5H_5)M(CO)_nMe$	$(\eta^5\text{-}C_5H_4EMe_3)M(CO)_nMe$
M = Mo, E = Sn	10	90
M = Mo, E = Pb	50	50
M = W, E = Sn	10	90
M = W, E = Pb	30	70
M = Fe, E = Sn	90	10

[a] Relative amounts determined by ^1H NMR.

taining the previously known $(\eta^5\text{-}C_5H_5)M(CO)_nMe$. The relative percentage of migration to cleavage reactions for the trimethyl complexes are reported in Table III.

The migration of the trisubstituted lead groups is of interest since the starting complexes $(\eta^5\text{-}C_5H_5)M(CO)_nPbR_3$ have been shown to be prone to both thermal and photochemical decomposition that involves an alkyl or aryl migration to the transition-metal center (eq 3), or disproportionation (eq 4).[13]

$$(\eta^5\text{-}C_5H_5)Mo(CO)_3PbMe_3 \xrightarrow{h\nu} (\eta^5\text{-}C_5H_5)Mo(CO)_3Me + PbMe_4 \quad (3)$$

$$2(\eta^5\text{-}C_5H_5)W(CO)_3PbEt_3 \xrightarrow{h\nu} [(\eta^5\text{-}C_5H_5)W(CO)_3]_2PbEt_2 + PbEt_4 \quad (4)$$

The migration to the cyclopentadienyl ring is one of the very few chemical reactions of the R_3Pb complexes that retains the R_3Pb group intact.

Treatment of all of the triphenyl- and trimethyltin and triphenyl- and trimethyllead complexes with n-BuLi as the base resulted exclusively in the cleavage of the metal–Sn or metal–Pb bond. In the case of the trimethyl derivatives such reactions led to the formation of trimethyl-n-butyltin and -lead derivatives along with the lithium salt of the corresponding cyclopentadienylcarbonylate (eq 5).

$$(\eta^5\text{-}C_5H_5)W(CO)_3SnMe_3 \xrightarrow{1.\ n\text{-BuLi}} [(\eta^5\text{-}C_5H_5)W(CO)_3]^-Li^+ + Me_3Sn\text{-}n\text{-}Bu \quad (5)$$

The various $[(\eta^5\text{-}C_5H_5)M(CO)_n]^-Li^+$ metalates (M = Fe, Mo, W) were characterized by treatment with methyl iodide and comparison of the resulting methyl derivatives with authentic materials.[14]

The transition metal–tin and –lead cleavage reactions above are related to various transmetalation equilibria of organotin and organolead compounds illustrated generally in eq 6.[15,16]

$$R_4E + R'Li \rightleftharpoons R_3ER' + RLi \quad (6)$$

Specific reactions are described in eq 7–9 for both tin and lead compounds.[17-19]

$$Ph_3SnCH_2C(Me){=}CH_2 + PhLi \rightarrow Ph_4Sn + CH_2{=}C(Me)CH_2Li \quad (7)$$

$$(C_6H_5)_3Pb(p\text{-}BrC_6H_4) + C_6H_5Li \rightarrow (C_6H_5)_4Pb + (p\text{-}BrC_6H_4)Li \quad (8)$$

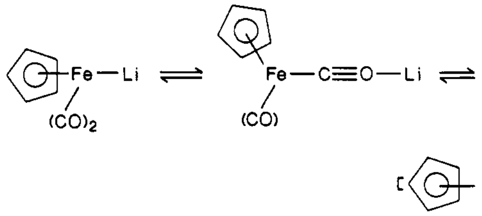
$$n\text{-}Bu_3SnCH{=}CH_2 + PhLi \rightarrow n\text{-}Bu_3SnPh + CH_2{=}CHLi \quad (9)$$

While such reactions are observed for both tin and lead, the silicon and germanium analogues do not readily exhibit such transmetalations, a situation that parallels the lack of transition metal–silicon and –germanium bond cleavage reactions in the present study. In our studies the transmetalations occur exclusively with the formation of the transition metalate; no clear evidence has thus far been observed for the formation of alkyl- or aryllithium salts and butyl (or amido) tin- or lead–transition metal complexes (eq 10).

$$(\eta^5\text{-}C_5H_5)M(CO)_3ER_3 + n\text{-}BuLi \not\rightarrow (\eta^5\text{-}C_5H_5)M(CO)_3ER_2(n\text{-}Bu) + RLi \quad (10)$$

The confusing chemistry noted from the reactions of $(\eta^5\text{-}C_5H_5)Fe(CO)_2PbPh_3$ with both LDA and n-BuLi may involve such reactions since many products are observed.

The infrared spectra of the various metalate intermediates obtained during the migration reactions provided interesting data concerning the nature of the ion pairing in the salts $[(\eta^5\text{-}C_5H_4R)Fe(CO)_2]^-Li^+$.[20,21] In general ion pairing of such systems has been shown to involve three major ion pair structures as noted below.



In each case where an R_3E group had migrated from the Fe atom to the cyclopentadienyl ring the infrared spectrum of the intermediate salt exhibited a markedly lower concentration of the tight ion pair involving a direct Fe–Li interaction with ν(CO) at 1878 and 1810 cm^{-1}. This may be associated with a steric factor at the Fe atom; however, regardless of the exact reason, the difference in IR provides a useful indicator of the nature of the reaction occurring upon addition of LDA or n-BuLi to the various $(\eta^5\text{-}C_5H_5)Fe(CO)_2ER_3$ complexes in THF.

Summary

a. Triphenylgermyl, -stannyl, and -plumbyl derivatives of the cyclopentadienyl carbonyl derivatives of Fe, Mo, and W readily migrate to the cyclopentadienyl ring when treated with LDA. An exception to this is the unclear chemistry of $(\eta^5\text{-}C_5H_5)Fe(CO)_2PbPh_3$.

b. Trimethylgermyl, -stannyl, and -plumbyl derivatives also migrate, but in the case of the stannyl and plumbyl derivatives the yields are much lower, and competition with transition metal–tin and –lead bond cleavage is observed, the latter being in general predominant.

c. Use of n-butyllithium in place of LDA has no effect upon germyl group migration but results exclusively in transition metal–tin and –lead bond cleavage.

d. It appears that steric factors, as well as basicity, could be important in determining the outcome of the base treatment reaction. Decreasing the steric constraint at the

---

(13) Pannell, K. H.; Kapoor, R. N. *J. Organomet. Chem.* **1984**, *269*, 59; 1981, *214*, 47. Pannell, K. H. *J. Organomet. Chem.* **1980**, *198*, 37.

(14) Piper, T. S.; Wilkinson, G. *J. Inorg. Nucl. Chem.* **1956**, *3*, 104.

(15) Shapiro, H.; Frey, F. W. *The Organic Compounds of Lead*; Wiley-Interscience Publishers: New York, 1968; Chapter VI.

(16) Poller, R. C. *The Chemistry of Organotin Compunds*; Academic Press: New York, 1970; Chapter 3.

(17) Seyferth, D.; Weiner, M. A. *J. Org. Chem.* **1961**, *26*, 4797.

(18) Zhadanov, G. S.; Kocheshkov, *Obshch. Khim., Akad. Nauk SSSR* **1953**, *1*, 285; *Chem. Abstr.* **1955**, *49*, 913.

(19) Seyferth, D.; Weiner, M. A. *J. Am. Chem. Soc.* **1961**, *83*, 3583.

(20) Pannell, K. H.; Jackson, D. *J. Am. Chem. Soc.* **1976**, *98*, 4443.

(21) Nitay, M.; Rosenblum, M. *J. Organomet. Chem.* **1977**, *136*, C23.

group 14 Sn or Pb atom increases the possibility of the transmetalation reaction as noted by the increasing amount of such reactions in the order EPh$_3$/LDA < EMe$_3$/LDA < EMe$_3$(EPh$_3$)/*n*-BuLi.

Acknowledgment. This research was supported by the Robert A. Welch Foundation, Houston, TX, and a Texas Advanced Technology Research Award.

Registry No. (η^5-C$_5$H$_4$GeMe$_3$)Fe(CO)$_2$Me, 118318-54-0; (η^5-C$_5$H$_4$GeMe$_3$)Mo(CO)$_3$Me, 118318-55-1; (η^5-C$_5$H$_4$GeMe$_3$)W(CO)$_3$Me, 118318-56-2; (η^5-C$_5$H$_4$GePh$_3$)Fe(CO)$_2$Me, 118318-57-3; (η^5-C$_5$H$_4$SnMe$_3$)Fe(CO)$_2$Me, 118318-58-4; (η^5-C$_5$H$_4$SnPh$_3$)Fe(CO)$_2$Me, 118318-59-5; (η^5-C$_5$H$_4$SnPh$_3$)Mo(CO)$_3$Me, 118334-33-1; (η^5-C$_5$H$_4$SnPh$_3$)W(CO)$_3$Me, 118318-60-8; (η^5-C$_5$H$_4$PbPh$_3$)Mo(CO)$_3$Me, 118318-61-9; (η^5-C$_5$H$_4$PbPh$_3$)W(CO)$_3$Me, 118318-62-0; (η^5-C$_5$H$_4$SnMe$_3$)Mo(CO)$_3$Me, 118318-63-1; (η^5-C$_5$H$_4$PbMe$_3$)Mo(CO)$_3$Me, 118318-64-2; (η^5-C$_5$H$_4$SnMe$_3$)W(CO)$_3$Me, 118318-65-3; (η^5-C$_5$H$_4$PbMe$_3$)W(CO)$_3$Me, 118318-66-4; (η^5-C$_5$H$_5$)Mo(CO)$_3$Me, 12082-25-6; (η^5-C$_5$H$_5$)W(CO)$_3$Me, 12082-27-8; (η^5-C$_5$H$_5$)Fe(CO)$_2$Me, 12080-06-7; (η^5-C$_5$H$_5$)Fe(CO)$_2$GeMe$_3$, 32054-63-0; (η^5-C$_5$H$_5$)Mo(CO)$_3$GeMe$_3$, 33306-91-1; (η^5-C$_5$H$_5$)W(CO)$_3$GeMe$_3$, 33306-93-3; (η^5-C$_5$H$_5$)Fe(CO)$_2$GePh$_3$, 32824-70-7; (η^5-C$_5$H$_5$)Fe(CO)$_2$SnMe$_3$, 12084-36-5; (η^5-C$_5$H$_5$)Fe(CO$_2$)SnPh$_3$, 12132-09-1; (η^5-C$_5$H$_5$)Mo(CO)$_3$SnPh$_3$, 12100-85-5; (η^5-C$_5$H$_5$)W(CO)$_3$SnPh$_3$, 12100-87-7; (η^5-C$_5$H$_5$)Mo(CO)$_3$PbPh$_3$, 12100-86-6; (η^5-C$_5$H$_5$)W(CO)$_2$PbPh$_3$, 12100-88-8; (η^5-C$_5$H$_5$)Mo(CO)$_3$SnMe$_3$, 12214-92-5; (η^5-C$_5$H$_5$)Mo(CO)$_3$PbMe$_3$, 12093-28-6; (η^5-C$_5$H$_5$)W(CO)$_3$SnMe$_3$, 12093-29-7; (η^5-C$_5$H$_5$)W(CO)$_3$PbMe$_3$, 79110-54-6; (η^5-C$_5$H$_5$)Fe(CO)$_2$PbPh$_3$, 12132-08-0.

Photochemical Substitution of Ethene and H/D Exchange in (η^5-Cyclopentadienyl)bis(ethene)rhodium

Simon T. Belt, Simon B. Duckett, David M. Haddleton,[1] and Robin N. Perutz*

Department of Chemistry, University of York, York YO1 5DD, U.K.

Received July 27, 1988

Photolysis of CpRh(C$_2$H$_4$)$_2$ (Cp = η^5-C$_5$H$_5$; 1) in benzene or toluene solution in the presence of substrates, L, leads to the formation of substitution products CpRh(C$_2$H$_4$)L and CpRhL$_2$. When L = Me$_2$SO and CH$_3$CN, only monosubstituted products are observed, but for other ligands (Ph$_3$P, CO, Bu^{t}NC, alkenes) both mono- and disubstituted products are formed. With 1,3-butadiene as the entering ligand, CpRh(C$_2$H$_4$)(η^2-C$_4$H$_6$) is formed prior to CpRh(η^4-C$_4$H$_6$). Conversion of the η^2-butadiene to the η^4-butadiene complex can be achieved photochemically or thermally. When CO or Bu^{t}NC are the substrates, dinuclear complexes (CpRhL)$_2$(μ-L) are formed in addition to substitution products. The photolysis method effects (a) the introduction of ligands that otherwise substitute only above 100 °C (Ph$_3$P, Me$_2$SO, alkenes), (b) the formation of labile complexes which cannot be formed by thermal methods (cyclohexene, CH$_3$CN, η^2-butadiene), and (c) the formation of the new dinuclear complex [CpRh(Bu^{t}NC)]$_2$(μ-Bu^{t}NC). For the labile complexes photolysis at low temperature is employed, since the products decompose at or below room temperature. Evidence is presented for the formation of CpRh(C$_2$H$_4$)(η^2-toluene) on photolysis at 193 K in toluene solution. An alternative route to substitution products involves photochemical conversion of 1 in CH$_3$CN to CpRh(C$_2$H$_4$)(CH$_3$CN) at 253 K followed by addition of ligand. The photochemical reactions are consistent with the mechanism deduced from earlier flash photolysis and matrix isolation experiments in which CpRh(C$_2$H$_4$) and CpRh(C$_2$H$_4$)S (S = solvent) act as intermediates. Photolysis with a C$_2$D$_4$ atmosphere demonstrates the existence of an additional pathway which causes H/D exchange within the ethene ligand. This pathway probably involves a vinyl hydride isomer of 1 as an unstable intermediate. There is no evidence for H/D exchange with the solvent. The complexes CpRh(C$_2$H$_4$)L (L = Me$_2$SO, CH$_3$CN, CH$_2$=CHSiMe$_3$) have a substantially higher barrier to rotation about the rhodium–ethene bond than has been reported for other complexes of this type. The dinuclear photoproduct [CpRh(Bu^{t}NC)]$_2$(μ-Bu^{t}NC) exhibits two fluxional processes, first interconversion of two conformers by internal rotation about the CN bond of the bridging isonitrile ($\Delta G^\ddagger = 45.7 \pm 1.6$ kJ mol^{-1}) and second exchange of bridging and terminal isonitriles ($\Delta G^\ddagger = 61.8 \pm 0.8$ kJ mol^{-1}).

Introduction

In a pioneering series of studies, Cramer showed that CpRh(C$_2$H$_4$)$_2$ (Cp = η^5-C$_5$H$_5$; 1), an 18-electron complex, is inert to substitution by alkenes (no exchange with ethene after 5 h at 100 °C), whereas (acac)Rh(C$_2$H$_4$)$_2$ (acac = pentan-2,4-dionato) with a 16-electron configuration is substitution-labile (half-life at −50 °C for exchange of ethene, 10^{-2} s).[2] Closer examination of the rates of reaction with donor ligands shows that the reactions fall into several distinct groups. Alkenes and dienes, Ph$_3$E (E = P, As, Sb), and AsEt$_3$ displace ethene at about 115–130 °C; P(OR)$_3$ (R = Et, Ph, *o*-tolyl) and PR'$_3$ (R' = Et, *n*-Bu) react rapidly at 100 °C; PMe$_3$ and phosphaalkynes react at room temperature; PF$_3$, SO$_2$, and C$_2$(CN)$_4$ react well below room temperature.[3,4] It was demonstrated from the independence of the rate on the concentration of the entering ligand that the slowest group reacted by a mechanism involving dissociation of ethene from 1. This dissociation has an activation energy of 130 kJ mol^{-1} in the gas phase. In contrast, the rates of the faster reactions were ligand dependent. At the most extreme, SO$_2$ and PF$_3$ were argued to react by an electrophilic mechanism, in which the rhodium complex acted as the nucleophile.

---

(1) Present address: ICI Chemicals and Polymers Group, Runcorn, U.K. No reprints available.

(2) Cramer, R. *J. Am. Chem. Soc.* **1967**, *89*, 4621; **1972**, *94*, 5681.

(3) Cramer, R. *J. Am. Chem. Soc.* **1967**, *89*, 5377. Cramer, R.; Seiwell, L. P. *J. Organomet. Chem.* **1975**, *92*, 245. Nixon, J. F.; Pinkerton, A. A. *Ibid.* **1972**, *37*, C47.

(4) Hitchcock, P. B.; Mohd, M. J.; Nixon, J. F. *J. Chem. Soc., Chem. Commun.* **1986**, 737.

0276-7333/89/2308-0748$01.50/0 © 1989 American Chemical Society